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# CHEMICAL SCIENCES

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# Canadian Journal of Research

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## PRODUCTION AND PROPERTIES OF 2,3-BUTANEDIOL

### XXVII. CRYSTALLINE ESTERS SUITABLE FOR IDENTIFICATION AND ESTIMATION OF THE ISOMERIC 2,3-BUTANEDIOLS[1]


BY FLORENCE M. ROBERTSON[2] AND A. C. NEISH[2]



### Abstract

The monoacid phthalates, di-*p*-nitrobenzoates, di-*m*-nitrobenzoates, di-3,5-dinitrobenzoates, di-*p*-bromobenzoates, and di-*p*-methoxybenzoates of *levo*-, and *meso*- and *dl*-2,3-butanediol were prepared to find which derivatives had the best properties for the identification of 2,3-butanediol isomers in a mixture. These are new compounds with the exception of the *levo*- and *dl*-monoacid phthalates and the *meso*-di-*p*-bromobenzoate. A procedure is given by which the optical isomers present in a 1 gm. sample of 2,3-butanediol can be identified, and the relative amounts of each estimated. They are converted to the di-*p*-nitrobenzoates, dissolved in chloroform, polarized to determine the concentration of the optically active isomers, and then fractionally crystallized for identification and estimation of relative amounts of the *dl*- and *meso*-esters.


### Introduction

2,3-Butanediol exists as *levo*-, *dextro*-, and *meso*-isomers all of which are known to be produced by bacterial fermentation. Thus *Aerobacillus polymyxa* is known to produce the *levo*-form to the practical exclusion of the other isomers (3, 9) while *Aerobacter aerogenes* has long been known to produce a mixture of the *meso*- and *dextro*-isomers, with the former predominating (8). A number of other species of bacteria are known to produce 2,3-butanediol (1, 5) and many more remain to be investigated. It is desirable to know, not only that a given species produces 2,3-butanediol, but also which isomer or mixture of isomers is formed. This information is important since the *meso*- and *levo*-isomers differ in their physical and chemical properties and consequently may have different industrial potentialities.

The purpose of the present investigation was to develop a procedure for the positive identification of the 2,3-butanediol and at the same time to estimate the relative amounts of each isomer. The best method of identifying simple organic compounds is by determining the melting point of the unknown mixed with a known authentic sample. Consequently a number of crystalline esters of *levo*-, *meso*- and *dl*-2,3-butanediol were prepared to find which would have the best properties, i.e., which would have convenient melting points


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and show the largest difference in melting points between the different isomers. Since the *dextro*-isomer should be identical with the *levo*-isomer in all properties, except the sign of rotation, it is not necessary to prepare its esters for this purpose.

In a previous work some success in separating 2,3-butanediol isomers was attained using the monoacid phthalates (3). Since the yields are small, based on the 2,3-butanediol used, these esters are not of much value for small-scale work. Good yields of diesters were obtained by reacting with benzoyl halide derivatives in pyridine. The melting points of the esters prepared in this way are shown in Table I. The monoacid phthalates are included for comparison.

TABLE I

MELTING POINTS OF ESTERS OF THE ISOMERIC 2,3-BUTANEDIOLS

| Ester | Melting point, ° C. | | |
|---|---|---|---|
| | *Meso*-isomer | *Levo*-isomer | Racemic mixture |
| Monoacid phthalate | 124.0–124.5 | 115.5–116.0 | 145.5–146.0 |
| Di-*p*-nitrobenzoate | 193.0–193.5 | 143.0–143.5 | 128.0–128.5 |
| Di-*m*-nitrobenzoate | 211.0–211.5 | 139.0–139.5 | 128.0–128.5 |
| Di-3,5-dinitrobenzoate | 247.0–247.5 | 212.0–212.5 | 185.0–186.0 |
| Di-*p*-bromobenzoate | 139.5–140.0 | 64.5– 65.0 | 79.0– 79.5 |
| Di-*m*-bromobenzoate | 67.0– 67.5 | Oil | 61.0– 61.5 |
| Di-*p*-methoxybenzoate | 150.0–150.5 | 85.0– 85.5 | 89.5– 90.0 |

Most of the compounds in this table have been prepared for the first time. The di-*p*-bromobenzoates of the *meso*- and *dl*-2,3-butanediol were first described by Wilson and Lucas (11). They reported the *dl* derivative to have a melting point of 204° to 209° C. instead of 79.0° to 79.5° C. as found in the present investigation. It seems likely that the compound they obtained was *p*-bromobenzoic anhydride since we also obtained some of this high melting compound in addition to the diol ester (see Experimental section for details).*

The optical rotations of the *levo*-diesters are shown in Table II. The di-*p*-nitrobenzoates were chosen as the most suitable of these esters for the purpose of identification because of the convenient melting point range, high specific rotation, ease of preparation, and ready availability of the reagent. The procedure for preparation of these esters was refined to ensure removal of water and other readily volatile hydroxyl compounds, and when applied to mixtures of 2,3-butanediol isomers, yields of approximately 90% of the isomeric diesters were obtained. It was found that these could be separated fairly well by four to six fractional crystallizations from acetone–water.

** Professor Lucas has brought our attention (A.C.N.) to an error in a previous paper in this series; cf. Can. J. Research B, 25; 70-79 (1947)—Table I. The optical rotation of the acetal of levo-2,3-butanediol should be −10.8° instead of −21.8°. This error is due to failure to reduce a reading made in a 2 dm. tube to 1 dm. when calculating the specific rotation. Other figures in this table, where a similar mistake may have been made, have been checked and found to be correct.*

TABLE II

SPECIFIC ROTATIONS OF *levo*-2,3-BUTANEDIOL ESTERS

| Ester | Solvent | Concentration, % | Specific rotation, $(\alpha)_D^{25}$ |
|---|---|---|---|
| Monoacid phthalate | Methanol | 20 | −16.0 (28° C.) |
| Di-*p*-bromobenzoate | Acetone | 5.0 | −43.0 |
| Di-3,5-dinitrobenzoate | Acetone | 1.0 | −36.0 |
| Di-*m*-nitrobenzoate | Acetone | 5.0 | −22.0 |
| Di-*p*-methoxybenzoate | Acetone | 5.0 | −29.2 |
| Di-*p*-nitrobenzoate | Acetone | 5.0 | −41.2 |
| " | Dioxane | 4.0 | −33.5 |
| " | Dioxane | 3.0 + 1.0 *meso* | −34.0 |
| " | Dioxane | 2.0 + 2.0 *meso* | −33.0 |
| " | Dioxane | 1.0 + 3.0 *meso* | −33.0 |
| " | Chloroform | 4.0 | −51.0* |
| " | Chloroform | 3.0 + 1.0 *meso* | −52.0 |
| " | Chloroform | 2.0 + 2.0 *meso* | −52.0 |

* *Observed rotation was −1.00 at 35° C. and −1.02 at 22° C. This shows relatively low sensitivity to temperature variation.*

Some results obtained on known mixtures of the pure diol isomers (1 gm. samples) are shown in Table III. It will be noted that the *meso*-isomer is

TABLE III

ESTIMATION OF 2,3-BUTANEDIOL ISOMERS BY FRACTIONAL CRYSTALLIZATION OF THE DI-*p*-NITROBENZOATES

(All isomers were estimated gravimetrically; polarimetric determinations of the *levo*-isomer were not made)

| Weight of mixed ester, gm. | Esters recovered as crystals, % | Composition of original diol mixture, % | Composition estimated from fractional crystallization, % |
|---|---|---|---|
| 3.90 | 94 | 21 *levo*<br>77 *meso*<br>2 *dl* | 15 *levo*<br>80 *meso*<br>8 *dl* |
| 4.25 | 94 | 28 *levo*<br>70 *meso*<br>2 *dl* | 23 *levo*<br>69 *meso*<br>8 *dl* |
| 4.20 | 93 | 51 *levo*<br>48 *meso*<br>1 *dl* | 47 *levo*<br>49 *meso*<br>1 *dl* |
| 4.30 | 96 | 70 *levo*<br>29 *meso*<br>1 *dl* | 71 *levo*<br>29 *meso*<br>no *dl* |
| 4.00 | 93 | 75 *levo*<br>24 *meso*<br>1 *dl* | 78 *levo*<br>22 *meso*<br>no *dl* |

readily separated from the rest but the separation of the *levo-* and *dl*-forms from each other is more difficult. If crystallization is allowed to occur slowly the *levo-* and *dl*-isomers crystallize in different forms which can be separated by hand. The isomers are distinguished by the microscopic appearance of the crystal masses rather than by reference to any particular crystal system. The *levo*-isomer has invariably given transparent masses while the *dl*-crystals are so small and densely clumped that the masses are opaque. When carefully recrystallized the *levo*-isomer will give large (1 mm. by 3 mm.) hexagonal prisms but sometimes tetragons are obtained instead. The *meso*-isomer and racemic mixture have always given such dense clusters that it is difficult to distinguish the form of the individual crystals. Sometimes crystals that appear to be pure *dl* are obtained which, in spite of the fact that they show the correct melting point, are found to contain approximately 25% of the *levo*-isomer, by polarization (see Table IV).

TABLE IV

FRACTIONAL CRYSTALLIZATION OF MIXTURES OF THE DI-*p*-NITROBENZOATES OF *levo-* AND *dl*-2,3-BUTANEDIOL

| Composition of diol mixture, % | Composition found by fractional crystallization, % | |
|---|---|---|
| | (*a*) By relying on m.p. only | (*b*) By correcting apparent *dl* for 25% *levo* |
| 31 *l* + 69 *dl* | 6 *l* + 94 *dl* | 29 *l* + 71 *dl* |
| 51 *l* + 49 *dl* | 29 *l* + 71 *dl* | 47 *l* + 53 *dl* |
| 70 *l* + 30 *dl* | 63 *l* + 37 *dl* | 72 *l* + 28 *dl* |

The amount of *levo-* (or *dextro-*) isomer can be estimated by polarization of the mixed esters dissolved in acetone, dioxane, or chloroform. The last solvent is preferred because of the higher specific rotation (Table II). Some results obtained on known mixtures are shown in Table V. These show that no detectable separation of isomers occurs during the esterification or precipitation of the esters. It is also noteworthy that the *levo*-2,3-butanediol produced by *Aerobacillus polymyxa* (last row, Table V) yielded no detectable amount of the *meso*-isomer on subsequent fractional crystallization. In the procedure finally adopted the mixed esters are first dissolved in chloroform, polarized, and then fractionally crystallized from acetone–water. This gives a fairly accurate determination of the optically active isomer, positive identification of the isomers present, and allows the relative amounts of *meso-* and *dl*-2,3-butanediol to be estimated. The degree of accuracy varies with the composition of the mixture. Details are given in the Experimental section.

The application of this procedure to fermentations would be facilitated by development of a more convenient method for recovering and purifying 2,3-butanediol from 100 ml. of the aqueous liquor. At present it is obtained from one to two liters by ether extraction and purified by distillation of 10 to 20 gm.

TABLE V

ESTIMATION OF *levo*-2,3-BUTANEDIOL BY POLARIZATION OF THE DI-*p*-NITROBENZOATES

| Isomers in mixture | Per cent *levo*-isomer | |
|---|---|---|
| | Present | Found |
| *Levo* and *dl* | 31.0<br>70.0 | 31.0<br>70.0 |
| *Levo* and *meso* | 28.5<br>34.0<br>69.0<br>70.5<br>70.5 | 28.0<br>34.5<br>69.5<br>70.0<br>72.5 |
| *Levo* and *meso* with 1% of *dl** | 63.0<br>60.0 | 62.0<br>60.0 |
| *Levo* and *meso* with 2% of *dl** | 32.0<br>22.0 | 31.0<br>20.0 |
| Pure *levo** | 100.0<br>100.0 | 100.0<br>99.0 |

** Diols in a 1% solution in ethyl ether at start.*

## Experimental

*Materials*

The *dl*-2,3-butanediol was prepared from Phillips Petroleum Company research grade butene-2 by the method of Wilson and Lucas (11), modified by the use of monochlorourea in place of calcium hypochlorite, as a source of hypochlorous acid. This butene gave a good yield of the *cis*-epoxybutane but a rather low yield of the *trans*-isomer. Hence *meso*-2,3-butanediol was prepared by purification of the *meso-dextro* mixture produced by fermentation of molasses with *Aerobacter aerogenes*. This mixture was converted to the acetone ketals, which were separated by distillation and hydrolyzed as previously described (4). The *levo*-2,3-butanediol, obtained from the fermentation of wheat by *Aerobacillus polymyxa* in the pilot plant operated by this Division, was purified by distillation through a Stedman column.

Reagents used in esterifying the isomeric 2,3-butanediols were: Eastman's phthalic anhydride, *p*-nitrobenzoyl chloride, and *m*-bromobenzoyl chloride; *p*-bromobenzoyl chloride and *p*-methoxybenzoyl chloride were obtained from Republic Laboratories. Reagent grade pyridine was used.

*Analytical Methods*

The equivalent weights of the monoacid phthalates were determined by titration of the free acid group with standard sodium hydroxide, in methanol–water, to the phenolphthalein end point. The equivalent weights of the other esters were determined by measuring the 2,3-butanediol liberated by

hydrolysis with alkali since this gave more reliable results than determination of the acid groups freed. A weighed sample of the ester was saponified by refluxing with a known excess of sodium hydroxide, the solution was neutralized with standard acid, oxidized with an excess of sodium periodate, and the unused periodate determined by the method of Rappaport, Reifer, and Weinmann (6). Duplicate analyses agreed within 1%, and were averaged. The 3,5-dinitrobenzoates were difficult to analyze since they were difficult to saponify and yielded very dark solutions. Addition of ethanol improved the saponification, which requires three hours, but it was found difficult to obtain good results for the *levo*-ester. Hence it was analyzed for nitrogen by the Dumas method to establish its structure as that of a diester.

Carbon and hydrogen were determined by the well known dry combustion procedure while bromine was estimated by Umhoefer's method (7). When the latter procedure was used with *p*-bromobenzoic anhydride it was found necessary to reflux 3.5 hr. with frequent stirring to effect complete dehalogenation because of the low solubility of this anhydride.

*Monoacid Phthalates of meso- and dl-2,3-Butanediol*

These were prepared by treatment of 2,3-butanediol (25 ml.) with sodium (1 gm.) followed by phthalic anhydride (7.4 gm.) as previously described for the *levo*-isomer (3). Both *meso*- and *dl*-esters were obtained in 60% yield. The melting point of the *dl*-ester agreed with that previously found for the sample isolated from a mixture consisting chiefly of the *levo*-isomer (3). The melting points are listed in Table I. Equivalent weight, calc.: 238; found: *meso*, 239; *dl*, 238.

*General Method of Preparing Substituted Dibenzoates of 2,3-Butanediol*

Some preliminary experiments with the Schotten–Baumann procedure were tried but better yields were obtained with pyridine. For the preparation of the esters listed below, the sample of 2,3-butanediol (1 to 2 gm.) was heated on a steam bath for one hour with a 25% excess of the theoretical requirement of acyl halide and enough pyridine to dissolve the reactants. The reaction mixture was then cooled to room temperature, poured into a solution of 5% sodium carbonate, and the precipitated ester filtered off, washed thoroughly with water, and purified by recrystallization from acetone, methanol, or ethanol. Esters melting above 200° C. were recrystallized from mixtures of nitrobenzene and ethanol or anisole and ligroin.

Melting points of the esters prepared by this procedure are listed in Table I and the optical rotation of the *levo*-isomers in Table II. A description of this method as applied to each type of ester follows. A more refined procedure for preparation of the *p*-nitrobenzoates is given in the section on examination of a mixture of 2,3-butanediol isomers.

*Di-p-nitrobenzoates and Di-m-nitrobenzoates*

The di-*p*-nitrobenzoates and di-*m*-nitrobenzoates of 2,3-butanediol crystallized readily and were obtained in yields of 90 to 95% of the theoretical value. The following values for the equivalent weight were found. Calc. for $C_{18}H_{16}O_8N_2$, 194. Found: di-*p*-nitrobenzoate:—*levo*, 196, *meso*, 195; *dl*, 196; di-*m*-nitrobenzoate:—*levo*, 193; *meso*, 196; *dl*, 197.

*Di-3,5-dinitrobenzoates*

The di-3,5-dinitrobenzoates were obtained in low yields (35 to 40%) even when the reaction time was increased from one to five hours. Because of their great insolubility in most solvents, the compounds were difficult to purify. A mixture of anisole and ligroin was found to be most suitable for the recrystallization of these esters. Equivalent weight:—calc. for $C_{18}H_{14}O_{12}N_4$, 239; found: *meso*, 236; *dl*, 239. Nitrogen content of the *levo*-ester:—calc. 11.71%; found: 11.71, 11.88%

*Di-p-methoxybenzoates*

The di-*p*-methoxybenzoates of *l*- and *dl*-2,3-butanediol precipitated as oils that were difficult to crystallize. Crystallization of these two compounds was effected by slowly dissolving the well chilled oil in methanol or ethanol. If crystals did not form during the solution process, they came out upon addition of a few drops of water to the solution. The *meso*-ester, having a higher melting point, crystallized without difficulty. Molecular weight: calc. for $C_{20}H_{22}O_6$, 179; found: *levo*, 180; *meso*, 181; *dl*, 180. Yields of these esters were in general 85 to 90%.

*Di-m-bromobenzoates*

The di-*m*-bromobenzoates were obtained in crystalline form with great difficulty, they crystallized very slowly even when relatively pure. The original crystalline *dl*- and *meso*-esters were obtained only after their oils had been allowed to stand for several days in the refrigerator, with occasional stirring and addition of a little solvent or a few drops of water to induce crystallization. The *levo*-compound was never obtained in crystalline form during the course of these experiments. The equivalent weight:—calc. for $C_{18}H_{16}O_4Br_2$, 228; found: *meso*, 227; *dl*, 231.

*Di-p-bromobenzoates*

The di-*p*-bromobenzoates of *dl*- and *l*-2,3-butanediol crystallized slowly, but the *meso*-isomer, because of its higher melting point, was obtained in crystalline form without difficulty. Yields were 75 to 80% of the theoretical. Equivalent weight:—calc. for $C_{18}H_{16}O_4Br_2$, 228; found: *levo*, 228; *meso*, 230; *dl*, 229. Because of the discrepancy between the melting point of the di-*p*-bromobenzoate of *dl*-2,3-butanediol found in this laboratory (79.0° to 79.5° C.) and the value (204° to 209° C.) given by Wilson and Lucas (11), a

bromine analysis was carried out on the material believed to be the di-*p*-bromobenzoate of *dl*-2,3-butanediol. Calc.: Br, 35.1%. Found: 34.9, 34.9%. This analysis, coupled with the quantitative yield of 2,3-butanediol obtained on saponification, establishes these compounds as the di-*p*-bromobenzoates. The compound obtained by Wilson and Lucas was probably *p*-bromobenzoic anhydride as shown below.

*p-Bromobenzoic anhydride*

In the purification of the crude material obtained in the preparation of the di-*p*-bromobenzoates of both *meso*- and *dl*-2,3-butanediol, recrystallization of the material from acetone yielded in both cases a small number of flat, elongated, high melting crystals, easily separable from the hard, more compact, lower melting crystals of the esters. Further crystallization of the high melting materials from acetone gave in both cases white crystals, m.p. 219.0° to 219.5° C. The melting point of a mixture of the two was not depressed; this indicated that they were the same compound. The isomeric glycols did not contribute to the formation of this compound, since it was obtained when a mixture of 2 ml. of *p*-bromobenzoyl chloride and 10 ml. of pyridine was heated on the steam bath for one hour and poured into carbonate in the manner usually followed in the preparation of the esters. This compound was proved to be *p*-bromobenzoic anhydride by analysis and by a mixed melting point with a synthetic sample prepared by the method of Jackson and Rolfe (2). Calc. for $C_{14}H_8O_3Br_2$: C, 44.0; H, 2.10; Br, 41.6%. Found: C, 44.2, 44.0; H, 2.19, 2.23; Br, 41.2%.

Formation of this anhydride is probably caused by a small amount of water present in the reagents; treatment of an acyl halide with pyridine and water is a recognized procedure for preparing acid anhydrides (10).

*Identification and Estimation of 2,3-Butanediol Isomers in a Mixture*

A procedure has been developed that permits the identification and estimation of the 2,3-butanediol isomers in admixture. This is applicable to 1 gm. or less of distilled 2,3-butanediol which must be free of other hydroxyl compounds with higher boiling points than water. The mixture of isomers is esterified with *p*-nitrobenzoyl chloride, a known weight of the dried ester mixture polarized in chloroform, and the mixture then fractionally crystallized from acetone–water. The polarization gives a fairly accurate measure of any optically active isomer while the fractional crystallization gives an approximate measure of the relative amounts of *meso*-isomer and racemic mixture. This permits an exact identification of each isomer by means of a mixed melting point determination. The details of this procedure follow.

2,3-Butanediol (1 gm.), benzene (40 ml.), and a glass bead are placed in a 250 ml. Erlenmeyer flask fitted with a ground-glass joint. This is connected to a reflux condenser by means of an adapter which allows removal of the distillate. The first liquid to distill over is the milky benzene–water azeotrope.

The distillate is withdrawn until the vapor temperature reaches 78° C. and the refluxing continued 10 min. more to ensure removal of water. The flask is then cooled and anhydrous pyridine (25 ml.) and *p*-nitrobenzoyl chloride (5 gm.) are added. Distillation is resumed and continued until the total volume of solvent removed is approximately equal to the volume of benzene originally added (38 to 42 ml.). At this point the vapor temperature is usually 93° to 95° C. and the mixture is clear. The contents of the flask is then poured with vigorous stirring into 50 ml. of 6% sodium carbonate. Any lumps are broken up and the precipitate allowed to harden for at least two hours. This crude ester is then filtered off, washed with water, pressed between filter paper, and air-dried between clean dry filter papers overnight. The yield is usually better than 90% and the material reasonably pure. Half a gram of crude, powdered ester is weighed into a 25 ml. volumetric flask, dissolved in chloroform, and the solution made to volume. This solution is quickly filtered through a fluted filter into a 2 dm. polarimeter tube and polarized at room temperature. The observed rotation for the pure *levo-* or *dextro-p*-nitrobenzoate is $\pm$ 2.03° under these conditions. Since the specific rotation is independent of dilution (Table II) the per cent of optically active isomer present in excess of its enantiomer in any mixture equals

$$\frac{\text{(Observed rotation) } 100}{2.03}.$$

The approximate relative amounts of the *meso*-isomer and the racemic mixture are determined by fractional crystallization from acetone. The exact details vary with the composition of the mixture but the following directions serve as a guide. The crude ester (about 4 gm. from 1 gm. of 2,3-butanediol) is weighed to the nearest 0.01 gm. after having been dried in air overnight. The material is then dissolved in acetone, filtered while hot to remove impurities, and allowed to concentrate on the steam bath to a volume of about 20 ml. If, when the solution cools to room temperature, crystallization has not begun spontaneously, a few drops of water are added, and the resulting turbidity discharged by acetone. After a crop of crystals has stood in contact with the mother liquor for several hours, it is filtered off and washed with acetone. The mother liquor and washings are combined, concentrated, and further crystallization induced. Each ester is identified by its melting point. Usually four to six crops allow the recovery of 90 to 95% of the crude material, from which a reliable estimate of the diol isomers can be made. Each crop is weighed to the nearest 0.01 gm. Even if more than one type of crystal can be seen in the mixture, recrystallization is seldom necessary. Instead, it is usually possible to separate the different components by hand and weigh each, or to estimate the relative contribution of each component. Calculations are based on the total amount of crystalline material recovered. Because of its much greater insolubility, the *meso*-ester tends to crystallize out first; the *levo-* and *dl*-esters have more nearly equal solubilities, and the ease with which they crystallize depends on the relative

amounts of each in the solution. The *levo*-ester itself crystallizes very slowly, even when a 'seed' is added, and its recovery is usually low. It has always crystallized from acetone–water mixtures as pale yellow, large transparent crystals, while the *meso*- and *dl*-esters usually give fine crystals which, in the case of the *dl*-mixture, often form button-shaped clumps.

However, the identification is based on the melting points of the crystals rather than on their appearance. It has been observed that the *levo*- and *dl*-forms sometimes give homogeneous crystal 'buttons' with the composition of three parts of *dl* to one of *levo*. These have the same melting point as the pure *dl*-crystals. Consequently these should be dissolved in chloroform and the purity checked polarimetrically.

The above procedure can be applied to a dilute solution of diol isomers in ether. When this is done the solution is concentrated in the esterification apparatus to a volume of 20 ml. before adding the benzene. No appreciable fractionation of isomers occurs here but there is some detectable separation of *levo*- and *meso*-isomers if a dilute aqueous solution is concentrated in this apparatus.

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# AN INVESTIGATION OF THE HYDRATES OF CALCIUM SULPHITE[1]

F. W. MATTHEWS AND A. O. MCINTOSH


## Abstract

Numerous references are found to the dihydrate of calcium sulphite, first reported by Muspratt in 1844. Repetition of this work showed no evidence of the formation of a dihydrate at room temperature but rather a hemihydrate. The optical properties reported for the dihydrate were those of the hemihydrate. The X-ray diffraction powder data reported for the anhydrous salt were found to check those of the hemihydrate. The hemihydrate was found to be stable to heating at 250° C. The dehydration to the anhydrous salt was accomplished by heating in a vacuum at 300° C.


## Introduction

Calcium sulphite is reported to form a dihydrate. An early reference to this is given by Muspratt (9). Röhrig (10) reported that the dihydrate was formed as fine granular crystals when calcium carbonate was treated with sulphur dioxide. This hydrate was reported to lose three-quarters of its water of hydration at 80° C. and all of it at 100° C. These results were supported by chemical analysis to prove the composition of the hydrates. Handbooks (5, p. 394; 7, p. 182) and textbooks on inorganic chemistry (3, p. 64; 8, p. 282) report this work as evidence for the dihydrate and the loss of two moles of water on heating to 100° C. Bichowsky (2) reported the dihydrate but stated that "Above temperatures somewhere near 160° C. the dihydrate is unstable in contact with water, presumably forming the semihydrate, $CaSO_3 \cdot 1/2H_2O$". His evidence for the composition of the hydrates is not given. Kelley and Moore (6) prepared calcium sulphite for specific heat measurements by reacting calcium carbonate and sulphur dioxide until no carbonate remained. After drying at 155° C. the product was found to contain 7.1% water. At 390° to 400° C. the water content was reduced to a negligible quantity. These authors state: "Röhrig's claim that calcium sulphite may be dehydrated to hemihydrate at 80° and to the anhydrous salt at 100° is incorrect." Romero and Gonzalez (11) report that in a 70% alcohol solution of a soluble sulphite, a hemihydrate is precipitated by calcium chloride. This salt is sufficiently stable to be used for the gravimetric quantitative estimation of sulphite.

Optical properties were measured on calcium sulphite prepared by Bichowsky (2) and are reported by Winchell (13, p. 215). X-ray diffraction data (1, 4) have been published for the anhydrous salt.

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[1] *Contribution from Central Research Laboratory, Canadian Industries Limited, McMasterville, Quebec. Presented before the Analytical Subject Division, Chemical Institute of Canada, Annual Conference, Montreal, June 1948.*

## Experimental

*Preparation of Calcium Sulphite Hemihydrate*

Calcium sulphite was prepared by (i) passing a stream of sulphur dioxide through a water suspension of calcium hydroxide; (ii) passing a stream of sulphur dioxide through a water suspension of calcium carbonate; (iii) dropping a solution of calcium chloride into a solution of sodium sulphite; (iv) evaporation of a solution of calcium acid sulphite prepared by carrying method (i) to complete solution of the hydroxide; (v) precipitation from a solution of the acid salt by the addition of ethyl alcohol. In all these methods the reactants were protected from contact with air to avoid oxidation of the sulphite to a sulphate.

The products of these reactions gave identical X-ray diffraction powder patterns which were in agreement with the data reported by Hanawalt *et al.* (1, 4) for the anhydrous salt. Chemical analysis showed these materials to contain from 8 to 10% water. This is more than that required for the hemihydrate (6.9%) and less than that required for the dihydrate (23.06%).

The products of these reactions were very fine powders which were unsuitable for analysis, or crystallographic study. In order to obtain larger crystals, calcium sulphite was prepared by diffusion in an H-shaped tube shown in Fig. 1. Two grams of reagent grade sodium sulphite was placed in the bottom of one leg and 2 gm. of reagent grade calcium chloride was placed in the bottom of the other. Boiled distilled water was blown from a wash bottle to the height of the cross tube in each leg and then sufficient water was added to fill the tubes. The openings were closed with rubber stoppers and the tube was placed in a beaker of water to dampen temperature fluctuations. After about two days the solids had dissolved and after four days crystals grew from the walls of the tubes, some of which were dislodged and fell to the bottom (see Fig. 2).

The powder diffraction pattern of the product grown by diffusion was identical with that of the products previously described.

Chemical analysis of the product grown by diffusion gave the following results:

| | | |
|---|---|---|
| Sulphite as $SO_2$ | 48.2% | by volumetric iodimetric method (12, p. 926) |
| Total S as $SO_2$ | 49.8% | by oxidation and gravimetric barium sulphate |
| CaO, total, | 43.1% | by oxalate precipitation of calcium. |

If we calculate the sulphite as calcium sulphite hemihydrate and assume the remainder of the sample to be calcium sulphate dihydrate the following composition is obtained—$CaSO_3 \cdot 1/2H_2O$ 97.2%, $CaSO_4 \cdot 2H_2O$ (by difference) 2.8%.

The equivalents on this composition are:

| | | |
|---|---|---|
| Calculated | CaO 43.1% | $SO_2$ 49.3% |
| Found | CaO 43.1% | $SO_2$ 49.8% |

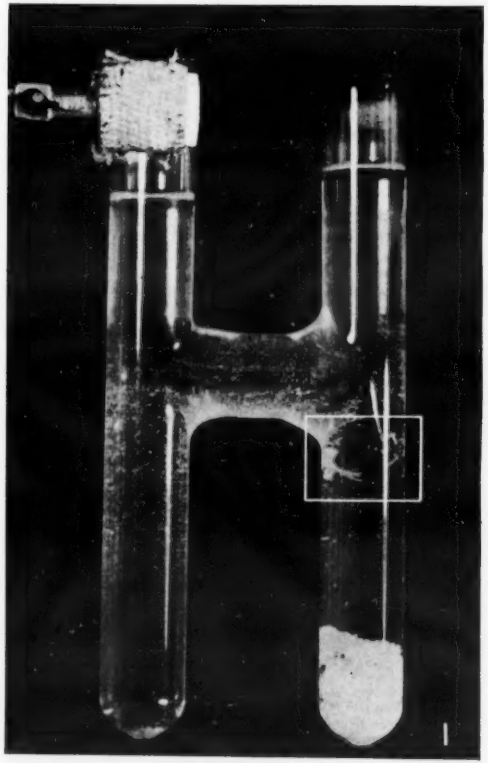

FIG. 1. *Apparatus for the growth of crystals by diffusion.* × *0.5. The area outlined is shown enlarged in Fig. 2.*
FIG. 2. *Crystals grown by diffusion.* × *2.8.*

The supposition that the sulphate is in the form of calcium sulphate dihydrate is justified if we consider that the sulphate is formed in the water medium during the growth of the crystals. If the crystals are oxidized later the formation of dihydrate is unlikely. The work of Romero and Gonzalez (11) indicates that in air the hemihydrate is stable to temperatures of 50° C.

The optical properties of the hemihydrate were determined as follows:

Refractive indices $\alpha = 1.596 \pm 0.002$

$\beta = 1.598 \pm 0.002$

$\gamma = 1.634 \pm 0.003$

Optic axial angle (+)2V is small

These are in substantial agreement with those given by Winchell (13, p. 215), for the dihydrate.

*Dehydration of the Hemihydrate*

To avoid oxidation, the dehydration of calcium sulphite was carried out in a vacuum (pressure of $10^{-3}$ mm. of mercury). In all cases a small amount of sulphate was found in the product. At temperatures up to 250° C. and under a vacuum of $10^{-3}$ mm. of mercury the water of crystallization was not removed from the hemihydrate, at 300° C. the water was removed slowly and at 400° C. more rapidly.

The sample for the dehydration experiments was prepared by reacting sodium sulphite with calcium chloride. The precipitate was dried in an air oven at 100° C. Previous work had shown that this preparation would contain a small amount of occluded water in addition to that required for the hemihydrate.

All heating was done in a closed tube furnace under a pressure of $10^{-3}$ mm. of mercury. The heating period was four hours at the temperature indicated. After each heating the sample was cooled under vacuum, removed from the furnace, and weighed.

| Temp. ° C. | | Loss in weight, % |
|---|---|---|
| 200 | 1st heat | 0.49 |
| 200 | 2nd heat | 0.73 |
| 250 | 1st heat | 1.38 |
| 250 | 2nd heat | 1.52 |
| 300 | 1st heat | 2.12 |
| 300 | 2nd heat | 4.68 |
| 300 | 3rd heat | 7.30 |
| 300 | 4th heat | 8.48 |

Chemical analysis of the product was as follows:—

| | | |
|---|---|---|
| Sulphite as $SO_2$ | 52.8% | by volumetric iodimetric method (12, p. 926). |
| Sulphate as $SO_3$ | 0.35% | by barium sulphate after removal of sulphite. |
| CaO, total | 45.9% | by oxalate precipitation of calcium. |

| | | |
|---|---|---|
| 52.8% $SO_2$ is equivalent to | 99.0% $CaSO_3$, which is equivalent to | 46.2% CaO |
| 0.35% $SO_3$ is equivalent to | 0.6% $CaSO_4$, which is equivalent to | 0.2% CaO |
| | 99.6% | 46.4% CaO |
| | | Found 45.9% CaO |

The X-ray diffraction powder data for the sample obtained on heating and for the hemihydrate are given in Table I.

TABLE I

X-RAY DIFFRACTION POWDER DATA

| $CaSO_3 \cdot 1/2H_2O$ | | $CaSO_3 \cdot 1/2H_2O$ | | $CaSO_3$ | |
|---|---|---|---|---|---|
| $d$ | $I/I_1$ | $d$ | $I/I_1$ | $d$ | $I/I_1$ |
| 5.55 | 0.40 | 1.74 | 0.05 | 5.50 | 0.02 |
| 5.30 | 0.10 | 1.67 | 0.50 | 3.80 | 0.05 |
| 4.81 | 0.10 | 1.615 | 0.50 | 3.49 | 0.05 |
| 4.26 | 0.02 | 1.575 | 0.02 | 3.12 | 1.00 |
| 3.77 | 0.90 | 1.560 | 0.02 | 2.90 | 0.60 |
| 3.14 | 1.00 | 1.517 | 0.15 | 2.79 | 0.05 |
| 2.96 | 0.40 | 1.474 | 0.15 | 2.71 | 0.05 |
| 2.80 | 0.20 | 1.441 | 0.02 | 2.61 | 0.05 |
| 2.65 | 0.10 | 1.411 | 0.05 | 2.53 | 0.80 |
| 2.61 | 0.60 | 1.358 | 0.02 | 2.34 | 0.20 |
| 2.39 | 0.05 | 1.329 | 0.02 | 2.11 | 0.40 |
| 2.23 | 0.02 | 1.2870 | 0.05 | 1.93 | 0.30 |
| 2.20 | 0.10 | 1.2726 | 0.02 | 1.82 | 0.15 |
| 2.14 | 0.05 | 1.2589 | 0.02 | 1.625 | 0.02 |
| 2.11 | 0.05 | 1.2420 | 0.10 | 1.565 | 0.05 |
| 2.05 | 0.10 | 1.2171 | 0.05 | 1.471 | 0.15 |
| 2.02 | 0.02 | 1.1980 | 0.05 | 1.402 | 0.02 |
| 1.95 | 0.15 | 1.1772 | 0.02 | 1.278 | 0.15 |
| 1.93 | 0.05 | 1.1620 | 0.02 | | |
| 1.84 | 0.60 | 1.1066 | 0.15 | | |
| 1.80 | 0.40 | 1.0812 | 0.10 | | |
| 1.77 | 0.10 | | | | |

Copper radiation, $\lambda = 1.54$ Å
Filter, nickel foil
Diameter of camera, 143.2 mm.
Cut off of camera, 15.0 Å
Collimator, 1.0 × 0.5 mm.
Specimen mount, wedge
Intensities, visual estimation

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# PHYSICAL PROPERTIES OF POLY-1,2-DIMETHYLETHYLENE PHTHALATE[1]

By R. W. Watson and N. H. Grace


## Abstract

The polyester derived from *levo*-2,3-butanediol and *o*-phthalic anhydride is moderately hard at a number average molecular weight of 660 ($DP = 3$), and at an average $DP$ of 4 is a brittle glass. Its hardness on the Brinell scale ranges from about 10 at $\overline{M}n = 880$, to 22–23 at $\overline{M}n = 2500$, where it equals the hardness of Lucite. Water absorption decreases with increasing molecular weight, and reaches a value of 0.08% in 430 days at 25° C. for a $DP$ 36 resin. A 50% solution of a solid $DP$ 4 resin ($\overline{M}n = 840$) in acetone has an absolute viscosity at 25° C. of 1.4 centipoises. Apparently molecular solutions are formed in common aromatic hydrocarbons, ketones, alkyl acetates, alcohols, ethers, and chlorinated solvents.


## Introduction

The preparation and properties of a polyester formed by direct esterification of 2,3-butylene glycol and phthalic anhydride were briefly reported in 1932 by Bradley (3). The product was described as of a softer nature than the soft resin from trimethylene glycol and phthalic anhydride. From the asymmetry of the chains, one might expect the dimethyl-substituted polyester to be a softer resin, at a given $DP$, than unsubstituted poly-ethylene phthalate. Actually it is many times as hard. Even the trimeric resin is semisolid at room temperature, and the physical properties change so rapidly at low extents of reaction that at a $DP$ of 4 it is a brittle glass. Since the pseudo-butylene glycol used in the earlier investigation (3) was not characterized it is difficult to account for the discrepancy. It seems improbable that such a marked physical difference should be attributable to the use of a different optical isomer, or mixture of optical isomers. Although the effects of isomer substitution have not as yet been thoroughly investigated, poly-*levo*-2,3-butanediyl *o*-phthalate emerges as a polyester with a new combination of physical properties.

## Experimental

A series of almost neutral reaction products was prepared from *levo*-2,3-butanediol ($n_D^{25} = 1.4310$, $[\alpha]_D = -13.0$) and an *o*-phthalic anhydride (Eastman 331). The reactants were heated at 180° to 210° C. for 2 to 120 hr. under deoxygenated nitrogen at atmospheric pressure, and subsequently for two or more hours at 210° C. (1 to 5 mm.). Continuation of the reaction *in vacuo* at an elevated temperature resulted in the production of almost

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neutral resins, with acid values from 1 to 6. Without purification their molecular weights were determined viscosimetrically using the equation

$$\ln \nu_r/c = 1.923 \times 10^{-5} \overline{M}n + 0.0176 \quad (16).$$

The acidic esters were made by adding to the neutral reaction products one-third of their weight of *o*-phthalic anhydride, and heating at 170° C. under carbon dioxide at atmospheric pressure for a further period of three hours. These resins were purified by washing three times in boiling water, dissolving in chloroform, drying, filtering, and removing the solvent *in vacuo* (5). The molecular weights of the acidic polyesters were determined by end-group titration.

For estimations of the Brinell hardness, disks 1 in. (2.54 cm.) in diameter, and 10 mm. in thickness, of purified acidic polyesters with known end-group molecular weights were prepared. Melted *in vacuo* to remove bubbles, the resins were cast in a special aluminum mold, and allowed to cool at room temperature. This method provided samples with smooth upper surfaces which would withstand loads up to 7.5 kgm. A series of readings at approximately 25° C. was made on each specimen using the standard 2.50 mm. ball in a Vickers' hardness testing machine (9). Casts were also made of four almost neutral reaction products which still contained small amounts of diol and free acid. It was often difficult with the optical equipment available to determine the true edge of the depression. Duplicate determinations on the same sample sometimes varied by as much as $\pm 5\%$, owing partly to the tendency of the material to fracture back from the actual impression line, and presumably also to local differences in hardness (7, 11). The results seem to be almost independent of minor variations in load.

Two purified acidic polyesters with number average molecular weights of 1000 and 10,870 were used in the general solubility determinations. Other resins, with approximate end-group molecular weights of 500, 1500, 2000, 2500, and 5000 were employed in two series of solutions in ether and methanol. About one gram of powdered resin was stirred into 5 ml. of solvent at room temperature, and reported as completely or partially soluble, or insoluble (6). The temperature of an air bath, at which the resin flowed 0.2 in. from the base of a thermometer bulb about 1 in. long, was taken as the flow point (6).

Water absorption was determined on thin disks, 2 in. (5.08 cm.) in diameter, and $\frac{1}{8}$ in. (0.32 cm.) thick, of purified acidic and neutral polyesters with known number average molecular weights. The resins were first melted *in vacuo* to remove bubbles, and a predetermined weight poured into a glass-bottomed mold, which was allowed to cool at room temperature. Edges of the casts were rounded after removal. The thickness of such disks varied by $\pm 0.02$ in., which somewhat exceeds the permissible variation in ASTM specifications for cast materials (1). Nevertheless, water absorption by duplicate disks of the same polyester checked to within $\pm 0.02\%$. Immersed on supports of

chromel wire in beakers of distilled water, held at 25.0 ± 0.1° C. in a thermostatically controlled bath, they were removed one at a time at the end of each 24 hr. period, wiped dry, and weighed immediately. The percentage increase in weight is reported as

$$\left(\frac{\text{Wet weight} - \text{dry weight}}{\text{Dry weight}}\right) \times 100.$$

Concentrated solution viscosities in acetone, benzene, and toluene ($d_4^{25}$ = 0.7852, 0.8734, and 0.8607 respectively) were measured for a reaction product with an average *DP* of about 11 ($\overline{Mn}$ = 2440). The Ostwald viscometer constant for this series ($K$ = 0.01067) was determined with pure benzene at 25.0° C., using 0.601 as the absolute viscosity of benzene at 25° C. (8). A purified polyester with an apparent molecular weight of 840 (viscosimetric) was also dissolved in 25 ml. portions of redistilled reagent acetone ($d_4^{25}$ = 0.7841, $n_D^{25}$ = 1.3562) to give 10, 20, 50, and 80% solutions (concentration = grams per 100 ml. of solvent). Constants for the two Ostwald–Cannon–Fenske viscometers ($K$ = 0.005176 and 0.01601, respectively) were determined with gas-free water at 25.00 ± 0.02° C., using 0.8937 centipoises as the absolute viscosity of water at 25° C.

## Results

The purified acidic resins (Table I and Fig. 1) possess Brinell numbers somewhat higher than those of the almost neutral reaction products, which still contain small amounts of diol and free acid. The hardness of the acidic

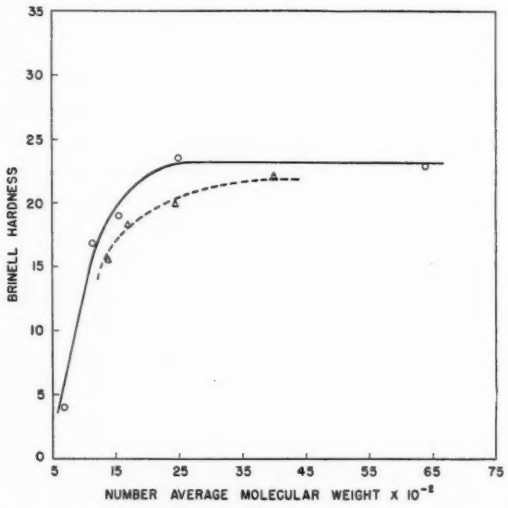


FIG. 1. *Relation between Brinell hardness at 25° C. and number average molecular weight; clear circles (full line)—pure acidic polyesters; triangles (broken line)—reaction products.*

TABLE I

BRINELL HARDNESS AND FLOW POINTS OF POLY-1,2-DIMETHYLETHYLENE PHTHALATE AND RELATED POLYESTERS

| Polyester | $\bar{M}n$ | Type of ester | Load, kgm. | Diameter of ball, mm. | Diameter of depression, mm. | Brinell hardness | Flow point, °C. |
|---|---|---|---|---|---|---|---|
| 1 | 680 | acidic | 3.5 | 2.50 | 1.028 | 4.0 | |
| 2 | 1130 | acidic | 3.5 | 2.50 | 0.508 | 16.8 | |
| 3 | 1380 | neutral | 7.0 | 2.50 | 0.533 | 15.4 | 105 |
| 4 | 1560 | acidic | 3.5 | 2.50 | 0.483 | 19.0 | |
| 5 | 1710 | neutral | 5.0 | 2.0 | 0.585 | 18.2 | 118 |
| 6 | 2440 | neutral | 3.5 | 2.0 | 0.461 | 20.0 | 134 |
| 7 | 2490 | acidic | 3.5 | 2.50 | 0.430 | 23.4 | |
| 8 | 4000ca. | neutral | 5.0 | 2.0 | 0.530 | 22.1 | 144 |
| 9 | 6370 | acidic | 3.5 | 2.50 | 0.437 | 22.8 | |
| 10 | 8000ca. | neutral | 7.5 | 2.0 | 0.575 | 28.4 | 155 |
| 11 | 2750 | ethylene phthalate | 3.5 | 2.50 | 1.150 | 3.2 | 78 |
| 11a | 880 | propylene phthalate | 1.0 | 2.50 | 1.615 | 0.8 | |
| 11b | 3900 | propylene phthalate | 3.5 | 2.50 | 0.537 | 14.8 | |

esters becomes approximately constant at an average *DP* of 11 to 12, where a Brinell number of about 23 is attained. By interpolation from Fig. 1, the acidic resins reach a Brinell hardness of about 10 at an average *DP* of 4 ($\bar{M}n = 880$). Lucite, poly-ethylene phthalate ($\bar{M}n = 2750$), and poly-propylene phthalate ($\bar{M}n = 3900$) had Brinell numbers, measured as described in the experimental section, of 22, 3, and 14.8 respectively. Ethylene, propylene, and 2,3-butylene glycols therefore form poly-phthalates which become increasingly harder as the degree of methyl substitution increases. This relation was apparently overlooked by Bradley (3), who extended the rule enunciated by Carothers and Arvin (5) to the methyl-substituted homologues of ethylene glycol. The lowest molecular weight previously reported for a solid polyester seems to be 2300 (5), whereas poly-*levo*-2,3-butanediyl *o*-phthalate is a thermoplastic solid (2) at 20° C. when the apparent molecular weight is $<880$.

The solubility relations are given in Table II. Decrease in solubility with increasing chain length is illustrated by the behavior in alcohols and ethers. Solid resins with a *DP* of 4 are generally soluble in both these solvent groups. At apparent molecular weights below about 1200, the resin is completely soluble in methanol and diethyl ether. Above this *DP* two phases are formed, with the lower phase becoming increasingly more viscous until virtual insolubility is reached in superpolyesters. Complete solvents for all size distributions include common aromatic hydrocarbons (except xylene), ketones, alkyl acetates, chlorinated solvents (except carbon tetrachloride) and dioxane. Esters at $\bar{M}n = 1000$ are soluble in methanol, allyl alcohol, diethyl ether, and aniline; partially soluble in other alcohols and ethers; and insoluble in saturated aliphatic hydrocarbons and water.

TABLE II

SOLUBILITIES OF POLY-1,2-DIMETHYLETHYLENE PHTHALATE

| Solvent | Completely soluble | Partially soluble | Insoluble |
|---|---|---|---|
| Benzene | X* | | |
| Toluene | X* | | |
| Xylene | | | X |
| Acetone | X* | | |
| Methyl ethyl ketone | X* | | |
| Cyclohexanone | X* | | |
| Methyl acetate | X* | | |
| Ethyl acetate | X* | | |
| Isopropyl acetate | X* | | |
| Butyl acetate | X* | | |
| Amyl acetate | X* | | |
| Methylene chloride | X* | | |
| Ethylene chloride | X* | | |
| Chloroform | X* | | |
| Carbon tetrachloride | | | X |
| Acetic acid | X* | | |
| Acetic anhydride | X* | | |
| Methanol | X | | X* |
| Ethanol | | X | |
| *n*-Propyl alcohol | | X | |
| Isopropyl alcohol | | X | |
| *sec*-Butyl alcohol | | X | |
| *n*-Amyl alcohol | | X | |
| Allyl alcohol | X | | |
| Cyclohexanol | | X | |
| *m*-Cresol | | X | |
| Diethyl ether | X | | X* |
| Isopropyl ether | | X | |
| Methyl phenyl ether | | X | |
| Dioxane | X* | | |
| Aniline | X | | |
| Carbon disulphide | | | X |
| Petroleum ether | | | X |
| Heptane | | | X |
| Methylcyclohexane | | | X |
| Water | | | X |
| Ethyl carbitol | X | | |
| Butyl carbitol | X | | |
| Butyl cellosolve | X | | |
| Turpentine | | | X |

X*—*Superpolyester* ($Mn$ = *10,870*).
X —*Alpha-polyester* ($\bar{M}n$ = *1000*).

The flow points of a series of reaction products containing small amounts of diol and free acid (Table I) range from 105° C. at an average *DP* of 6, to 155° C. at a *DP* of 36. Like the Brinell numbers, the flow points of purified acidic polyesters are somewhat higher, and range from 80° C. at *DP* 4 to 160° C. at *DP* 50.

The absolute viscosities of a series of concentrated solutions of a purified polyester ($\bar{M}n$ = 840), and of a reaction product ($\bar{M}n$ = 2440) in acetone, benzene, and toluene, are listed in Table V. In Fig. 3, log $\eta$ (centipoises)

is plotted against concentration in grams per 100 ml. of solvent. At a *DP* of 4 ($\overline{M}n$ = 840), a 50% solution in acetone at 25° C. has an absolute viscosity of 1.4 centipoises. At a *DP* of 11 ($\overline{M}n$ = 2440), solutions of the same concentration in acetone, benzene, and toluene at 25° C. have absolute viscosities of 3.5, 8.7, and 7.7 centipoises respectively.

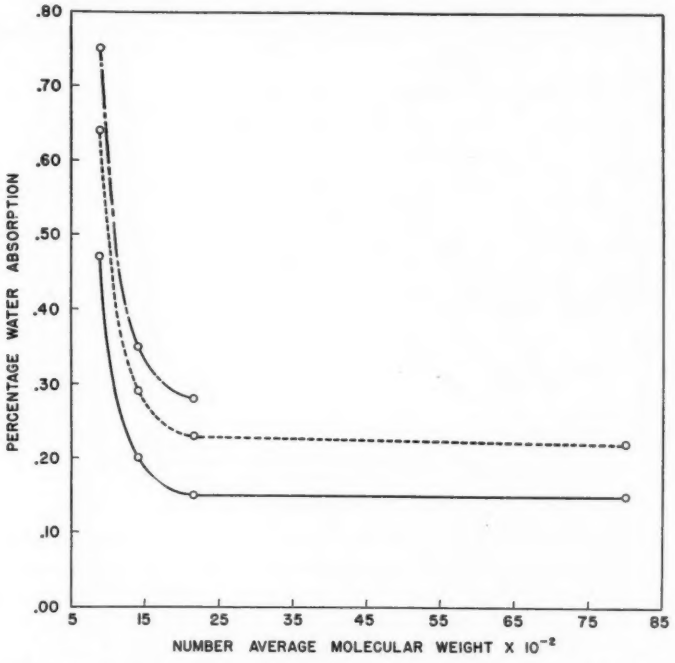


FIG. 2. *Dependence of water absorption at 25° C. on apparent molecular weight: immersion periods, 24 hr. (full line); 48 hr. (broken line); 72 hr. (dot-dash).*

TABLE III

PERCENTAGE WATER ABSORPTION OF NEUTRAL RESINS AT 25.0° C.

| Polyester | 12 | 13 | 14 | 15 |
|---|---|---|---|---|
| $\overline{M}n$ | 890 | 1400 | 2150 | 8000 ca. |
| Hours immersed | Increase in weight, % | | | |
| 24 | 0.47 | 0.20 | 0.15 | 0.15 |
| 48 | 0.64 | 0.29 | 0.23 | 0.22 |
| 72 | 0.75 | 0.35 | 0.28 | |
| 888 | | | | 0.79 |
| 912 | | 1.22 | 0.87 | |
| 936 | 2.18 | | | |

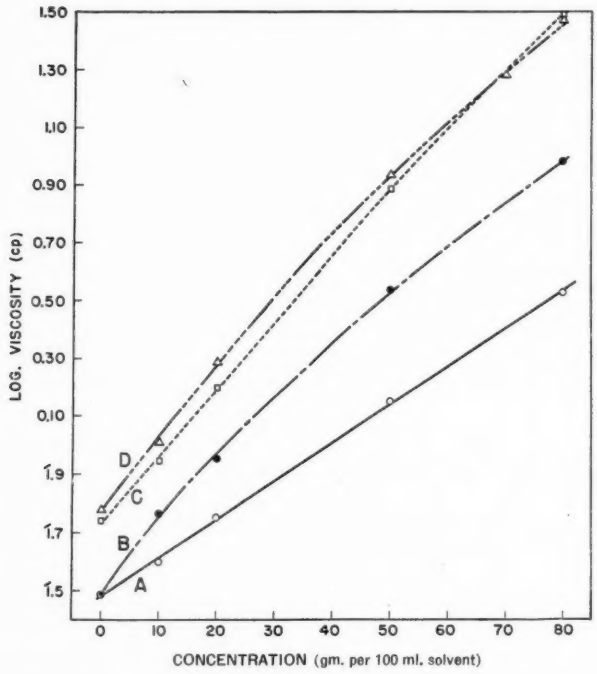


FIG. 3. *Log viscosity (centipoises) at 25° C. vs. concentration (gm. per 100 ml. solvent).*
*A. (Clear circles, full line) )—acetone; DP 4 resin ($\overline{M}n$ = 840).*
*B. (Solid circles, dot-dash)—acetone; DP 11 resin ($\overline{M}n$ = 2440).*
*C. (Squares, broken line)—toluene; DP 11 resin ($\overline{M}n$ = 2440).*
*D. (Triangles)—benzene; DP 11 resin ($\overline{M}n$ = 2440).*

The percentage increase in weight of the neutral esters, after immersion in water at 25° C., is given in Table III, and the dependence of water absorption on molecular weight is shown graphically in Fig. 2. The percentage water absorption decreases rapidly with increasing molecular weight up to an average *DP* of about 10, where it becomes almost constant. Resins with hydroxyl-ended chains remain clear indefinitely under water. The color, luster, and transparency of polyesters 12 to 15 (Table III) were unchanged after five weeks' immersion. On allowing resins with a *DP*> about 7 to dry after a period under water, numerous minute superficial cracks develop. This checking does not appear at lower degrees of polymerization. The surface of polyester 13 ($\overline{M}n$ = 1400) remained smooth on prolonged drying after 912 hr. immersion. At the end of a similar period, polyester 12 ($\overline{M}n$ = 890) was soft and pliable, clear, completely lacking in tackiness, and easily pulled into thin transparent films.

The percentage absorption of the acidic resins (Table IV) also decreases with increasing molecular weight, but not with the regularity observed in the neutral series. Moreover, the percentage increase in weight is higher for the

TABLE IV

PERCENTAGE WATER ABSORPTION OF ACIDIC POLYESTERS AT 25.0° C.

| Polyester | 16 | 17 | 18 | 19 | 20 |
|---|---|---|---|---|---|
| $\overline{Mn}$ | 1130 | 1560 | 2490 | 6370 | 11430 |
| Hours immersed | Increase in weight, % | | | | |
| 24 | 0.38 | 0.25 | 0.13 | 0.13 | 0.16 |
| 48 | 0.58 | 0.35 | 0.25 | 0.16 | 0.23 |
| 72 | 0.70 | | 0.33 | 0.20 | 0.28 |
| 96 | 0.78 | | 0.38 | 0.21 | |
| 120 | 0.89 | | 0.44 | 0.24 | |
| 144 | 0.95 | | 0.51 | 0.27 | |
| 168 | 1.00 | | 0.55 | 0.30 | |
| 192 | | | 0.61 | 0.34 | |
| 888 | | 1.76 | | | |
| 936 | | | | | 0.79 |
| 1032 | | | 1.43 | 1.24 | |

acidic group below a *DP* of 10. Up to a *DP* of at least 7 (polyesters 16 and 17), the surface of acidic resins soon becomes cloudy under water. After immersion for one week, polyester 16 ($\overline{Mn}$ = 1130) showed chalky white patches; and, after five weeks, scales and larger pieces had broken off, leaving a white surface. This effect decreased in polyester 17, and in the remaining three test specimens (18, 19, and 20), the luster and transparency were retained indefinitely, as noted for the neutral resins.

A much lower percentage absorption was shown by a neutral *DP* 36 resin ($\overline{Mn}$ = *ca.* 8000) cooled slowly from the melt. Three small disks, about ½ in. in diameter and 1/16 to 1/8 in. thick, were immersed in distilled water at room temperature (20° to 30° C.) for over a year. There was a slight and gradual absorption for several months, after which the weights remained almost constant. The maximum values after 430 days' immersion were 0.40%, 0.28%, and 0.08% respectively.

Specific gravities, determined pycnometrically, of two neutral resins, with number average molecular weights of 2440 and *ca.* 8000, were 1.228, and 1.250, respectively. The refractive indices, determined by the immersion method, of three purified acidic polyesters, with end-group molecular weights of 670, 1130, and 1560 were 1.543, 1.545, and 1.547, respectively. A purified neutral resin, with an apparent molecular weight (viscosimetric) of 890 had $n_D^{25} = 1.537$.

TABLE V

CONCENTRATED SOLUTION VISCOSITIES IN ACETONE, BENZENE, AND TOLUENE AT 25° C.

| Solvent | $\bar{M}n$ | Concentration, gm. per 100 ml. solvent | $K$ | $d_4^{25}$ | $t$, sec. | $\eta^{25} = K.d.t.$, cp |
|---|---|---|---|---|---|---|
| A. Acetone | 840 | 10.0 | 0.005176 | 0.8399 | 91.5 | 0.40 |
| " | " | 20.0 | " | 0.8610 | 127.2 | 0.57 |
| " | " | 50.0 | " | 0.9324 | 294.3 | 1.42 |
| " | " | 80.0 | " | 0.9824 | 666.2 | 3.39 |
| B. Acetone | 2440 | 10.0 | 0.01067 | 0.8228 | 66.3 | 0.58 |
| " | " | 20.0 | " | 0.8541 | 98.3 | 0.90 |
| " | " | 50.0 | " | 0.9308 | 347.5 | 3.45 |
| " | " | 80.0 | " | 0.9743 | 927.8 | 9.65 |
| C. Toluene | 2440 | 10.0 | " | 0.8902 | 93.3 | 0.89 |
| " | " | 20.0 | " | 0.9145 | 162.3 | 1.58 |
| " | " | 50.0 | " | 0.9714 | 741.0 | 7.68 |
| " | " | 80.0 | " | 1.014 | 2900 | 31.37 |
| D. Benzene | 2440 | 10.0 | " | 0.9010 | 106.8 | 1.03 |
| " | " | 20.0 | " | 0.9253 | 195.9 | 1.93 |
| " | " | 50.0 | " | 0.9828 | 826.4 | 8.67 |
| " | " | 70.0 | " | 1.0090 | 1796 | 19.36 |
| " | " | 80.0 | " | 1.0210 | 2747 | 29.93 |
| E. Toluene | 840 | 10.0 | 0.005176 | 0.8924 | 171.8 | 0.79 |
| " | " | 80.0 | 0.01601 | 1.017 | 1087 | 17.70 |

## Discussion

The predominant influence of molecular weight on flow point is evident if the values from Table I are plotted against the corresponding number average molecular weights. A curve is obtained which levels off at a $DP$ of about 40. Carothers has noted for a given crystalline polyester that the melting point usually increases with increasing molecular weight up to a certain value, after which it remains unchanged (4); and that melting points increase with the polarity of the structural unit. Both the increased hardness and the higher flow point in the dimethyl-substituted polyester point to increased interchain forces, as compared with those of unsubstituted poly-ethylene phthalate. At present it is difficult to express an opinion as to the mechanism of this reversal.

Among crystalline compounds, solubility is often strikingly changed by the substitution of lateral methyl groups. The greater solubility of hydrocarbons with methyl side chains may be traced to greater irregularity in their structure, and also to the fact that a methyl group is more strongly solvated than a methylene group (14). The fatty acid diesters of 1,2- and 1,3-butylene glycols are more easily soluble than esters of corresponding unsubstituted glycols (13). These well established qualitative rules help to explain the

increased solubilities of this polyester, as compared with those of poly-ethylene phthalate (5). The speed of solution and the viscosity data suggest the formation of true molecular solutions in acetone and chloroform, and probably also in the other solvents listed in Table II in which solubility is rapid and complete.

The wide variation in concentrated solution viscosities between the ketone and aromatic hydrocarbon solvents (Table V) may be associated with differences in solvation, since as much as one-half or more of the solution viscosity of a polymeric material may be ascribed to this effect (10). The low absolute viscosity combined with hardness at an average *DP* of 4, seem to confer on poly-1,2-dimethylethylene *o*-phthalate the lowest solution viscosity of any recorded solid polyester.

A possible interrelation between hardness and water absorption is indicated by the constancy which both these properties attain at about the same degree of polymerization. The unusually low absorption of the neutral polyester ($\overline{Mn}$ = ca. 8000), which was cooled slowly from the melt, may be associated with its greater hardness (Table I). Water apparently penetrates only a thin superficial layer of the harder polyesters. Conversion of the neutral resins in the presence of excess *o*-phthalic anhydride to acidic esters supports the view that the neutral chains are terminated by hydroxyl groups. Some factor, possibly related to the packing of the neutral chains may be responsible for the lower water absorption of the hydroxyl-ended esters, and for the conspicuous difference in their appearance after immersion in water.

The specific gravity (1.23 to 1.25), hardness, water absorption, and noticeable resistance to complete saponification in methanolic sodium hydroxide (15) are properties concordant with moderately dense packing. The observed luster follows from the comparatively high refractive index, which is slightly above that of borosilicate glass.

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# NOTES

## Note on the Hydrogenation of α-Methylnaphthalene

In the course of a program of work related to the determination of the oxidation mechanism of naphthenes (1), it was found desirable to synthesize an α-methyldecahydronaphthalene by the hydrogenation of α-methylnaphthalene. Literature does not record hydrides of α-methylnaphthalene, though some hydrides of naphthalene are known (2).

We have identified some products of the destructive hydrogenation of α-methylnaphthalene as well.

### Experimental*

Commercial α-methylnaphthalene was treated with sodium metal for one week at room temperature, then with adsorbent carbon near the boiling point for one hour, and filtered. A higher rate of hydrogenation was attained by such treatment.

The catalyst used was Raney nickel, prepared according to usual procedure (3).

Dehydrogenation of the hydrides was carried out by refluxing in the presence of 10% by weight of Raney nickel catalyst. Nitrogen gas was bubbled through the reaction mixture throughout the procedure.

1. *α-Methyldihydronaphthalene.*—α-Methylnaphthalene (50 gm.), and Raney nickel catalyst (5 gm.) were admitted to a rocking autoclave. Hydrogen was introduced to a pressure of 2000 p.s.i. The temperature was raised to 310° C. and maintained for four hours. Approximately 0.9 mole hydrogen per mole α-methylnaphthalene was absorbed. The straw-colored liquid was filtered, and fractionally distilled under diminished pressure. A fraction was separated; b.p. 111° to 111.5° C. (15 mm.), 235° C. (760 mm.), sp. gr.$\frac{22}{4}$ 0.977, $n_D^{20}$ 1.5764, yield 49%. Calc. for $C_{11}H_{12}$: C, 91; H, 8.38%. Found: C, 91.5; H, 8.28%. Dehydrogenation yielded α-methylnaphthalene. The liquid rapidly darkened in presence of air. It reacted avidly with concentrated sulphuric acid (96%).

2. *α-Methyltetrahydronaphthalene.*—The reaction mixture containing dihydro product was not removed from the autoclave, but was subjected to a second hydrogenation, under the same conditions of temperature, pressure. and time. Approximately 1.8 moles hydrogen per mole α-methylnaphthalene was absorbed. A colorless liquid was formed which was filtered and fractionally distilled under diminished pressure. A fraction was separated; b.p. 108° C. (15 mm.), 231° C. (760 mm.), sp. gr.$\frac{24}{4}$ 0.948, $n_D^{20}$ 1.5540, yield

* *All boiling points uncorrected.*

90%. Calc. for $C_{11}H_{14}$ : C, 90.3; H, 9.66%. Found: C, 90.2; H, 9.86%. Dehydrogenation yielded α-methylnaphthalene. The liquid reacted slowly with concentrated sulphuric acid (96%).

3. *α-Methyldecahydronaphthalenes, α-Methyloctahydronaphthalene, α-Methylhexahydronaphthalene.*—α-Methylnaphthalene (50 gm.) was hydrogenated under conditions described above, until no further absorption of hydrogen took place. This generally required three or four successive operations of four hour duration, with the admission of fresh catalyst after the second operation. Approximately 4.5 moles hydrogen per mole α-methylnaphthalene was absorbed. The colorless reaction mixture was fractionally distilled under diminished pressure. Fraction I separated; b.p. 89.5° to 89.7° C. (15 mm.), 208° C. (760 mm.), sp. gr.$\frac{24.4}{4}$ 0.8706, $n_D^{20}$ 1.4705, yield 30%. Calc. for α-methyldecahydronaphthalene, $C_{11}H_{20}$ : C, 86.8; H, 13.2%. Found C, 87.1; H, 13.1%. It dehydrogenated very slowly to α-methylnaphthalene. No appreciable reaction with concentrated sulphuric acid (96%) occurred.

Fraction II separated; b.p. 96.0° C. (15 mm.), 216° C. (760 mm.), sp. gr.$\frac{24.4}{4}$ 0.8811, $n_D^{20}$ 1.4798, yield 30%. Calc. for α-methyldecahydronaphthalene, $C_{11}H_{20}$ : C, 86.8; H, 13.2%. Found: C, 87.0; H, 13.0%. It dehydrogenated very slowly to α-methylnaphthalene. No appreciable reaction with concentrated sulphuric acid (96%) occurred.

Fraction III separated; b.p. 101° to 101.3° C. (15 mm.), 222° C. (760 mm.), sp. gr.$\frac{20}{4}$ 0.905, $n_D^{20}$ 1.5055, yield 5%. Calc. for α-methyloctahydronaphthalene, $C_{11}H_{18}$ : C, 87.9; H, 12.1%. Found: C, 87.8; H, 11.9%. It dehydrogenated slowly to α-methylnaphthalene and reacted only slowly with concentrated sulphuric acid (96%).

Fraction IV separated; b.p. 105° C. (15 mm.), 227° C. (760 mm.), sp. gr.$\frac{21}{4}$ 0.930, $n_D^{20}$ 1.5283, yield 5%. Calc. for α-methylhexahydronaphthalene, $C_{11}H_{16}$ : C, 89.1; H, 10.9%. Found: C, 89.3; H, 10.5%. It dehydrogenated slowly to α-methylnaphthalene and reacted only slowly with concentrated sulphuric acid (96%).

It is probable that the substances separated represent some geometrical isomers of α-methyldecahydronaphthalene.

## Destructive Hydrogenation of α-Methylnaphthalene

### Experimental*

α-Methylnaphthalene (50 gm.) and Raney nickel catalyst (5 gm.) were admitted to a stationary autoclave. Hydrogen was introduced to a pressure of 140 atm. The temperature was raised to 400° C. and maintained for five hours. This procedure was repeated until no further absorption of hydrogen was indicated. The colorless reaction mixture (40 gm.) was fractionally

* *All boiling points uncorrected.*

distilled through a Stedman column, at atmospheric pressure. Fraction I separated; b.p. 81° C. (760 mm.), sp. gr. $\frac{20}{4}$ 0.779, $n_D^{20}$ 1.428, yield 2%. Calc. for cyclohexane, $C_6H_{12}$ : C, 85.7; H, 14.3%. Found: C, 86.0; H, 14.1%.

Fraction II separated; b.p. 125° C. (760 mm.), sp. gr. $\frac{24}{4}$ 0.805, $n_D^{20}$ 1.436, yield 2%. Calc. for 1,2-dimethylcyclohexane, $C_8H_{16}$ : 85.7; H, 14.3%. Found: C, 85.9; H, 14.2%.

Fraction III separated; b.p. 153° C. (760 mm.), sp. gr. $\frac{22}{4}$ 0.788, $n_D^{20}$ 1.438, yield 5%. Calc. for 1-methyl-2-ethylcyclohexane, $C_9H_{18}$ : C, 85.7; H, 14.3%. Found: C, 85.7; H, 14.1%.

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